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This report is a summary of the results of an effort to understand the details of chemical bond activation on atomically clean transition metal single crystal surfaces. Modern experimental methods of surface science were employed and developed in this work. The following general classes of chemical bond activation (elementary reaction steps) have been studied on close packed planes of Ni, Pt, Pd, and Mo: O-H; HC-H; C-C; H₃C-OH; H₃-CN; H₃C-NH₂; H₃CN-H₂; H-CN; HC≡N; O-O; and certain of the bonds in a phosphonic ester.

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Final Technical Report
Organic Functional Group Reactivities at Metal Surfaces
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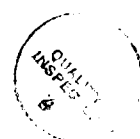
This is a summary of the results of a three year effort to understand the details of chemical bond activation on atomically clean transition metal single crystal surfaces. Modern experimental methods of surface science are employed and developed in this work. The following general classes of chemical bond activation (elementary reaction steps) have been studied on close packed planes of Ni, Pt, Pd, and Mo: O-H; HC-H; C-C; H₃C-OH; H₃-CN; H₃C-NH₂; H₃CN-H₂; H-CN; HC≡N; O-O; and certain of the bonds in a phosphonic ester. The connection to Army missions is mainly in understanding elementary steps in heterogeneous catalysis involving important functional groups which may be present in chemical agents.

A list of research highlights is given below:

- Bond scission sequence in the surface decomposition of CH₃CH₂OH on Ni(111) has been determined using Scanning Kinetic Spectroscopy, Temperature Programmed Desorption, and Deuterium Kinetic Isotope Effect methods. The sequence O-H, HC-H, and C-C has been observed for increasing temperature.
- The absence of C-O bond scission in H₃C-OH chemisorbed on Ni(111) has been determined unequivocally, clarifying earlier reports to the contrary.
- Functional group competition for X-H bond scission has been studied for H₃CNH₂ on Ni(111). The CH₃- group has been found to be the leading group, by a slight margin in temperature, in initiating the decomposition of monomethyl amine, in agreement with a recent study by another laboratory, just published. In addition, the complete decomposition of the molecule to H(a), C(a), and N(a) has been studied, and characteristic temperatures for each bond scission event have been determined.

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- Systematic comparison of HCN reaction channels on the Ni-group of transition metals under constant surface structure conditions [fcc-(111)]. The relative activity for HCN decomposition is $\text{Ni}(111) > \text{Pd}(111) > \text{Pt}(111)$. For HCN oxidation, the relative activity is $\text{Pt}(111) > \text{Pd}(111) > \text{Ni}(111)$.
- HCN decomposition on a Ni(111) surface has been characterized. At low HCN coverages, both C-H and C-N bond scission events have been observed. At higher HCN coverages, molecular HCN is stabilized. The reactivity of HCN on Ni(111) exhibits similar trends as observed in its fully-hydrogenated counterpart, CH_3NH_2 .
- The reactivity of Pt(111) and highly stepped Pt(112) surfaces have been compared for HCN decomposition. The stepped surface has been found to be more reactive catalytically as indicated by the recombination processes: $\text{H}(\text{a}) + \text{CN}(\text{a}) \rightarrow \text{HCN}(\text{g})$, and $2\text{CN}(\text{a}) \rightarrow \text{C}_2\text{N}_2(\text{g})$, and $2\text{H}(\text{a}) \rightarrow \text{H}_2(\text{g})$. C-N bond scission is not observed.
- First study of the details of HCN oxidation by adsorbed atomic O on a Pt(111) single crystal, despite the fact that HCN oxidation over Pt catalysts is considered to be the most convenient and least polluting catalytic oxidation route. An oxidation mechanism through an $\text{NCO}(\text{a})$ intermediate is postulated on kinetic grounds. It has also been demonstrated that the oxidation kinetics are favored on a stepped Pt(112) surface, compared to Pt(111).
- Discovery that surface peroxo (Pt-O_2) species are powerful oxidizing agents on Pt(111) for HCN oxidation. These species produce an enhancement of CO, CO_2 and H_2O yields in lower temperature reaction channels for coverages of $\text{O}_2(\text{a})$ which are equivalent to $\text{O}(\text{a})$ coverages used in control experiments.
- Discovery that monolayer quantities of $\text{CN}(\text{a})$ are effective reaction barriers for penetration of bulk-H from Pd(111) to the surface. The product, HCN, desorbs following this reaction.
- Discovery of the first transition metal catalyst system for the continuous catalytic oxidation of organophosphonate compounds. The basic reaction products have been characterized, and the surface composition of the catalyst has been determined in the presence and the absence of oxygen gas reactant. The catalyst is Mo, and the Mo(110) plane was studied. Reaction occurs at about 900 K, and a monolayer oxide surface is catalytically active. It is likely that the production of volatile phosphorus oxide(s) is rate controlling.

A list of the 15 research and review publications, divided into two categories is given below.

A. RESEARCH CONTRIBUTIONS

1. S. M. Gates, J. N. Russell, Jr., and J. T. Yates, Jr., "Bond Activation Sequence Observed in the Chemisorption and Surface Reaction of Ethanol on Ni(111)," *Surface Science*, 171, 111 (1986).
2. I. Chorkendorff, J. N. Russell, Jr., and J. T. Yates, Jr., "Surface Reaction Pathways of Methylamine on the Ni(111) Surface," *J. Chem. Phys.* 86(8), 4692 (1987).
3. J. N. Russell, Jr., I. Chorkendorff, and J. T. Yates, Jr., "Methanol Decomposition on Ni(111) - Investigation of the C-O Bond Scission Mechanisms," *Surface Sci.* 183 (1987) 316.
4. P. L. Hagans, I. Chorkendorff, and J. T. Yates, Jr., "SKS and TPD Study of the Adsorption and Decomposition of HCN on the Ni(111) Surface," *J. Phys. Chem.* 92 (1988) 471.
5. V. S. Smentkowski, P. Hagans, and J. T. Yates, Jr., "Study of the Catalytic Destruction of Dimethyl Methylphosphonate (DMMP): Oxidation Over Mo(110)," accepted *J. Phys. Chem.*
6. P. L. Hagans, X. Guo, I. Chorkendorff, A. Winkler, H. Siddiqui, and J. T. Yates, Jr., "Adsorption and Dissociation of HCN on the Pt(111) and Pt(112) Surfaces," accepted, *Surface Science*.
7. X. Guo, A. Winkler, P. L. Hagans, and J. T. Yates, Jr., "Oxidation of HCN on the Pt(111) and Pt(112) Surfaces," accepted, *Surface Science*.
8. X. Guo, A. Winkler, P. L. Hagans, and J. T. Yates, Jr., "Reactivity of Surface Peroxo Species: Oxidation of HCN on Pt(111)," accepted, *Surface Science*.
9. X. Guo, A. Hoffman, and J. T. Yates, Jr., "Reaction of Bulk Hydrogen in Pd(111) with Adsorbed CN: A Possible Controlled Barrier for Hydrogen Diffusion," submitted to *Surface Science*.
10. X. Guo, A. Hoffman, P. L. Hagans, and J. T. Yates, Jr., "Comparative Reactivities of Ni(111), Pd(111), and Pt(111) Surfaces for the Decomposition and Oxidation of HCN," submitted to *J. Am. Chem. Soc.*

B. REVIEW CONTRIBUTIONS

1. J. N. Russell, Jr., S. M. Gates, and J. T. Yates, Jr., "Scanning Kinetic Spectroscopy (SKS) - A Method for Studying Functional Group Reactivities in Heterogeneous Catalysis," Proceedings of 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, April 1986, p.335.
2. J. T. Yates, Jr., J. N. Russell, Jr., and S. M. Gates, "Kinetic and Spectroscopic Investigations of Surface Chemical Processes," "Chemistry and Physics of Solid Surfaces," Vol. VI," Springer-Verlag, Berlin-Heidelberg-New York (1986) p. 237.
3. I. Chorkendorff, P. L. Hagans, J. N. Russell, Jr., and J.T. Yates, Jr., "Scanning Kinetic Spectroscopy for Determination of Major Reaction Pathways on Single Crystals", 2nd Nordic Conference on Surface Science, Linköping University, Linköping, Sweden.
4. J. G. Ekerdt, K. J. Klabunde, J. R. Shapley, J. M. White, and J. T. Yates, Jr., "The Surface Chemistry of Organophosphorus Compounds", Journal of Physical Chemistry, 92, 6351 (1988).
5. J. T. Yates, Jr., "The Activation of Chemical Bonds at Surfaces," Solvay Conference on Chemistry and Physics at Surfaces, 1988, Proceedings, accepted.

The following people have been associated with the project and their current status is listed:

<u>Name</u>	<u>Status</u>
1. Dr. S. M. Gates	Permanent employee, IBM-Yorktown Heights
2. Dr. J. M. Russell, Jr.	Ph.D. (1987)
3. Dr. I. Chorkendorff	Professor, Denmark
4. Dr. Pat Hagans	Scientist, Dow Chemical
5. Mr. V. S. Smentkowski	2nd yr. graduate student, Pittsburgh
6. Mr. X. Guo	4th yr. graduate student, Pittsburgh

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